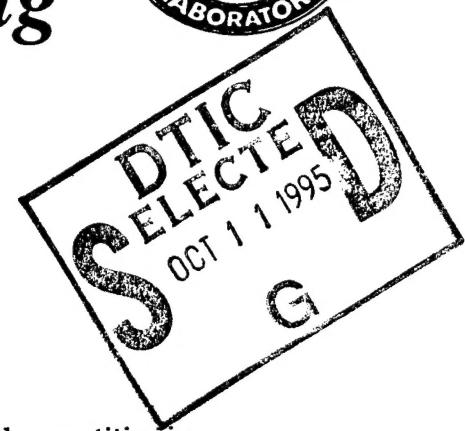




Environmental Effects of Dredging Technical Notes



Fluoranthene K_{DOC} in Sediment Pore Waters

Purpose

This note describes laboratory testing conducted to examine the partitioning of fluoranthene to dissolved organic carbon in the pore water of sediments.

Background

The U.S. Environmental Protection Agency (EPA) is authorized to develop and implement sediment quality criteria (SQC) under Section 304(a) of the Clean Water Act. Under this authority the EPA is proceeding with development of SQC for nonpolar organic compounds and metals. A major assumption in the current approach to SQC is that truly dissolved concentrations of hydrophobic organic contaminants (HOCs) in sediment pore water can be computed by assuming that K_{DOC} (partition coefficient normalized to colloidal plus dissolved organic carbon, DOC) equals K_{oc} (partition coefficient for sediment organic carbon).

The U.S. Army Corps of Engineers is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as the utility of equilibrium partitioning approaches for predicting toxicity. In the equilibrium partitioning approach, toxicity is related to pore water concentrations of contaminants. This study compared measured concentrations of truly dissolved fluoranthene to concentrations predicted by current models.

Additional Information

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Introduction

Concentrations of truly dissolved organic contaminants in sediment pore water are regarded as the contaminant fraction available for organism uptake (Landrum and others 1985; Kukkonen, McCarthy, and Oikari 1990). However, concentrations of truly dissolved organic contaminants in pore water are difficult to measure directly because organic contaminants are also associated with dissolved and colloidal organic matter (Carter and Suffet 1982, Chiou and others 1986, Kile and Chiou 1989).

Concentrations of truly dissolved organic contaminants in pore waters are commonly estimated (DiToro and others 1991) by assuming constant partitioning between pore water (truly dissolved) and organic carbon in pore water. However, DeWitt and others (1992) showed that the dissolved organic matter partitioning coefficient (K_{DOC}) was not constant in a base substrate amended with different sources of organic matter. In addition, the structure and composition of humic materials is known to affect K_{DOC} values of hydrophobic organic compounds (Gauthier, Seitz, and Grant 1987; McCarthy, Roberson, and Burrus 1989; Davis 1993). Brannon and others (1991) and Magee, Lion, and Lemley (1991) have shown that changing DOC composition was a primary cause of nonconstant partitioning during facilitated transport of HOCs. Although Brannon and others (1991) did not determine values of K_{DOC} , their data indicated that DOC had lower sorption potential than sediment organic carbon for polychlorinated biphenyls.

If K_{DOC} is not equivalent to K_{oc} , then many of the assumptions used in modeling interactions between HOCs and particulate and dissolved organic carbon in aquatic systems are invalid. This study was conducted to examine the constancy of K_{DOC} in sediment pore water and to compare measured values of K_{DOC} with computed values derived from K_{oc} .

Materials and Methods

Pore waters from 11 sediments were extracted under a nitrogen atmosphere to maintain anaerobic conditions (Brannon and others 1991). The pore water was stored in amber bottles until tested (within 1 day of sample generation). Separate subsamples were acidified with sulfuric acid and set aside for analysis of DOC.

Nine 10-ml aliquots of each pore water sample were removed and placed in a 25-ml glass centrifuge tube. Aliquots from each pore water were spiked with ^{14}C -labeled fluoranthene at three concentrations (0.127, 0.077, and 0.04 mg/L) in each of three replicates. The highest concentration was less than 50 percent of the aqueous solubility of fluoranthene cited in Verschueren (1983). Total fluoranthene in solution was determined by liquid scintillation-counting the original filtered leachate. Additional centrifugation removed the majority of colloidal-bound fluoranthene, while passage through the C-18 Sep-Pak provided a measure of the concentration of truly dissolved fluoranthene.

Truly dissolved means not associated with colloidal material and DOC remaining in the solution after centrifugation.

The total organic carbon (TOC) content of the centrifuged, filtered pore water was determined using a Shimadzu Total Organic Carbon Analyzer, model 5050. The TOC determined for the centrifuged, filtered pore water was designated as the DOC fraction and was used to calculate the K_{DOC} .

Results

The TOC concentration in pore waters ranged from 4.8 to 177 mg C/L (Table 1). Sediments from which the pore waters were obtained represented a range of sites and contents of TOC (Table 1).

Partitioning, or distribution of a hydrophobic organic compound between DOC and water at equilibrium, is mathematically described as follows:

$$K_{DOC} = C_{DOC}/C_W \quad (1)$$

Table 1. Sediment Total Organic Carbon (TOC), Pore Water Dissolved Organic Carbon (DOC) Concentrations, and Coefficients for Regression ($n = 11$) of Truly Dissolved and Bound Fluoranthene in Sediment Pore Water

| Sediment | Sediment TOC, % | Pore Water DOC, mg/L | Slope | Standard Error of Slope | Intercept | r^2 |
|--------------------------|-----------------|----------------------|---------|-------------------------|-----------|-------|
| Oakland Inner Harbor, CA | 0.34 | 4.8 | 36,000 | 6,400 | 536 | 0.84 |
| Richmond Harbor, CA | 0.49 | 9.1 | 55,100 | 11,700 | 444 | 0.76 |
| West Richmond Harbor, CA | 0.23 | 4.2 | 96,200 | 11,900 | -1,042 | 0.90 |
| Pinole Shoals, CA | 0.52 | 16.0 | 35,300 | 5,300 | -304 | 0.86 |
| Hamlet City Lake, NC | 4.76 | 7.2 | 106,300 | 4,200 | -54 | 0.99 |
| Browns Lake, MS | 0.84 | 13.0 | 86,700 | 9,700 | -277 | 0.92 |
| Eau Galle Lake, WI | 1.42 | 10.0 | 61,200 | 10,300 | -142 | 0.83 |
| Eau Plaine Lake, WI | 1.15 | 177.0 | 66,900 | 6,100 | 55 | 0.94 |
| Barataria Bay, LA | 21.18 | 79.0 | 42,035 | 2,800 | -220 | 0.97 |
| Swan Lake 1, MS | 2.37 | 42.0 | 44,200 | 3,900 | -275 | 0.95 |
| Swan Lake 4, MS | 2.24 | 15.0 | 14,600 | 2,200 | 655 | 0.89 |

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where

K_{DOC} = distribution coefficient, L/kg

C_{DOC} = concentration of contaminant sorbed to the dissolved organic carbon, mg/kg

C_W = truly dissolved aqueous phase fluoranthene concentration, mg/L

Values of K_{DOC} were computed by regression of sorbed (normalized to DOC concentrations) versus truly dissolved fluoranthene for all pore waters. Slopes, standard error of the slope, y-intercepts, and regression coefficients are also presented in Table 1. Error in estimates of the slopes averaged 13.4 percent for all sediment pore waters. Error included differences between replicates and experimental procedure. Regression coefficients were high, ranging from 0.76 to 0.99, as expected for linear isotherms.

Pore water K_{DOC} values for fluoranthene varied from 14,600 to 106,300 L/kg. This wide variation in K_{DOC} (a factor of 7.3) suggests that the *quality* of organic carbon in pore waters differed and affected K_{DOC} . This is further illustrated by the wide range of DOC normalized concentrations of sorbed fluoranthene that exists for a particular solution concentration of truly dissolved fluoranthene (Figure 1).

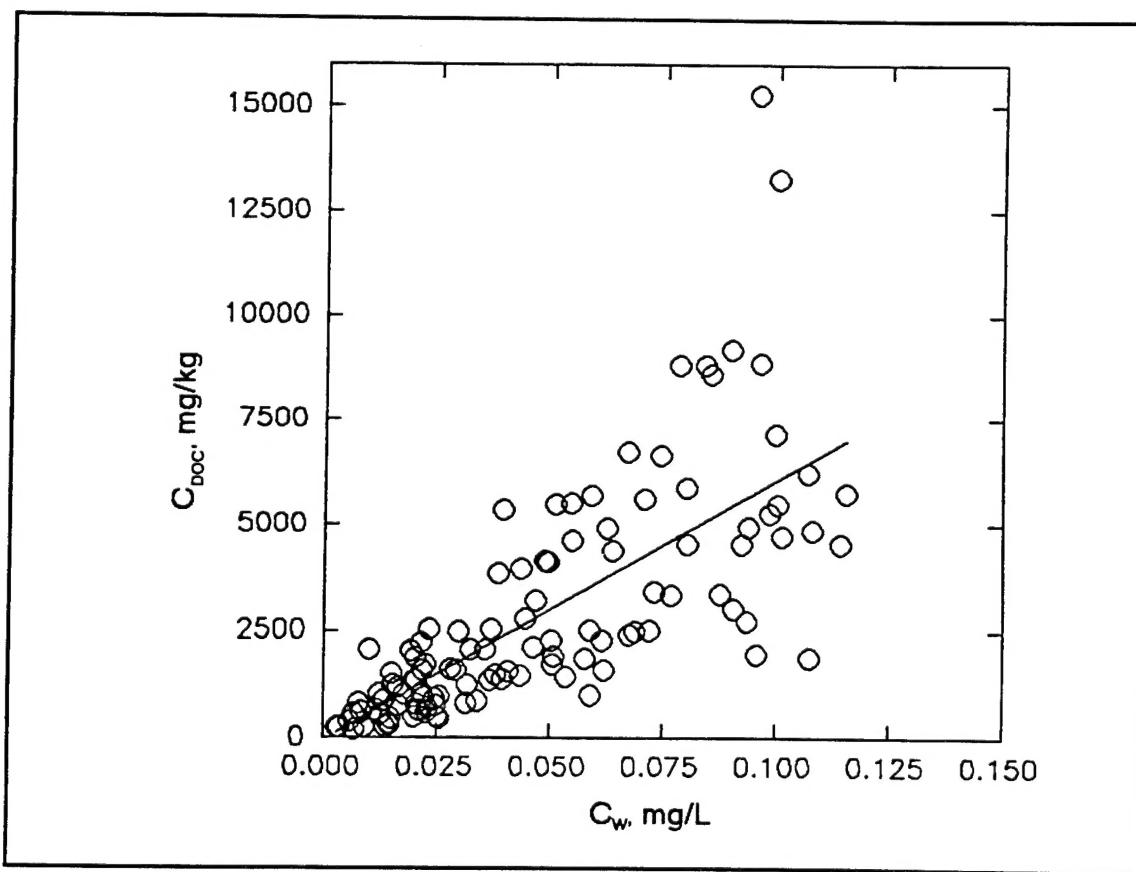


Figure 1. Truly dissolved (C_W) versus DOC normalized (C_{DOC}) fluoranthene concentrations in pore water

As pore water DOC concentrations increased, the fraction of bound fluoranthene increased and the fraction of truly dissolved fluoranthene decreased (Figure 2). The fraction of truly dissolved fluoranthene in solution ranged from approximately 5 to 80 percent of the total fluoranthene in the pore water. This resulted in a wide range of truly dissolved and sorbed fluoranthene concentrations in the experiment.

K_{DOC} was estimated using the common assumption that $K_{DOC} = K_{oc}$ (DiToro and others 1991). The estimated K_{oc} value was computed by substituting K_{ow} or $\log K_{ow}$ (octanol/water partition coefficient) for fluoranthene into the equation $K_{oc} = 0.411 K_{ow}$ (Karickhoff 1981) or $\log_{10} K_{oc} = 0.00028 + 0.983 \log_{10} K_{ow}$ (DiToro and others 1991), respectively. The value of $\log K_{ow} = 5.12$ for fluoranthene was derived by averaging fluoranthene K_{ow} values determined by De Bruijn and others (1989), 5.15, and the U.S. Environmental Protection Agency (1993), 5.09.

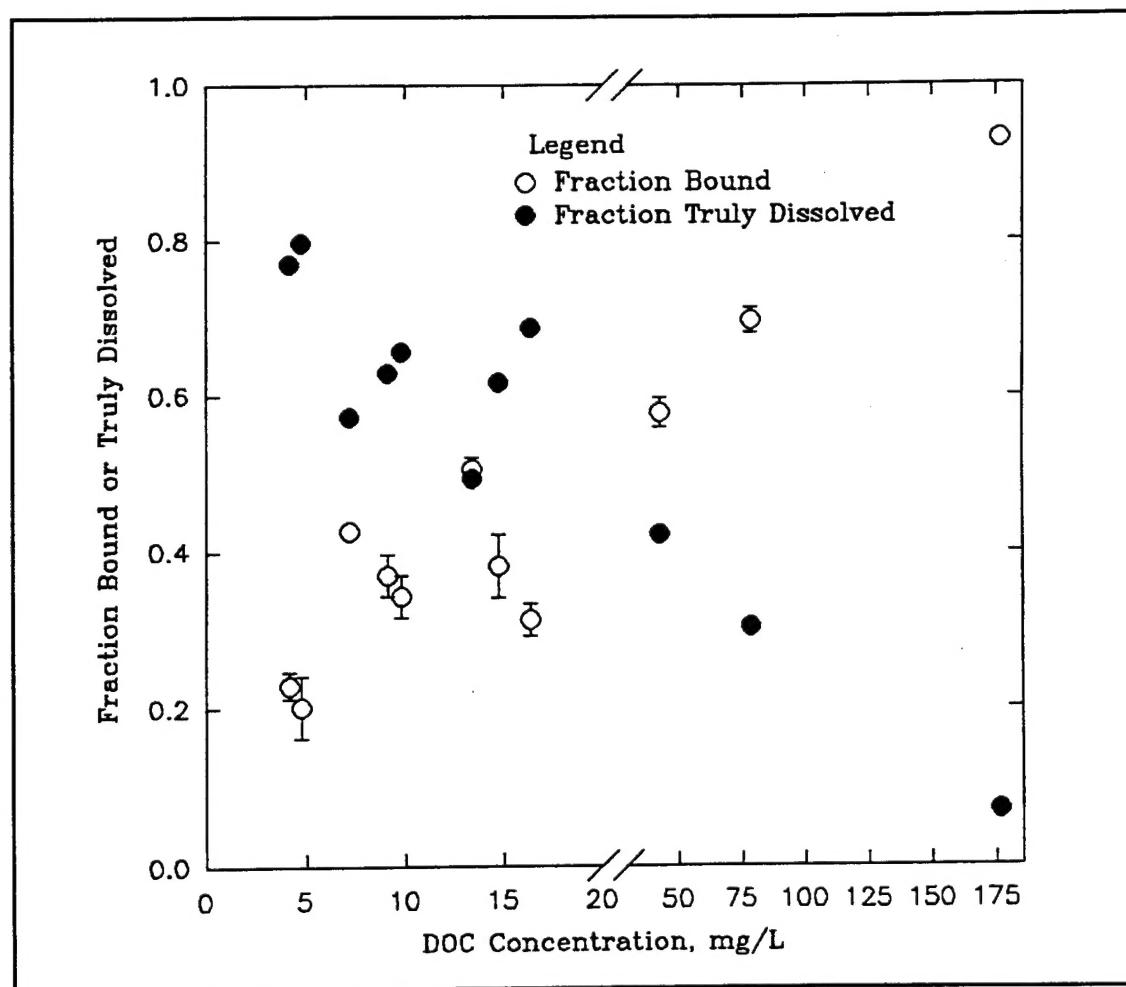


Figure 2. Fraction of bound and truly dissolved fluoranthene as a function of pore water DOC concentration

The measured values of K_{DOC} were consistently lower than the K_{DOC} value estimated using the method of DiToro and others (1991) (Figure 3). The method of Karickhoff (1981) over- and underestimated measured values of K_{DOC} . A particularly wide range of measured K_{DOC} values was observed below 20 mg DOC/L, where most of the pore water DOC values fell.

Concentrations of truly dissolved fluoranthene are related to that bound to dissolved organic matter by the equation (DiToro and others 1991):

$$C_{DOC} = m_{DOC} K_{DOC} C_d \quad (2)$$

where

C_{DOC} = concentration of fluoranthene associated with DOC, mg/L

m_{DOC} = concentration of DOC in solution, kg/L

K_{DOC} = DOC partitioning coefficient, L/kg

C_d = concentration of dissolved fluoranthene, mg/L

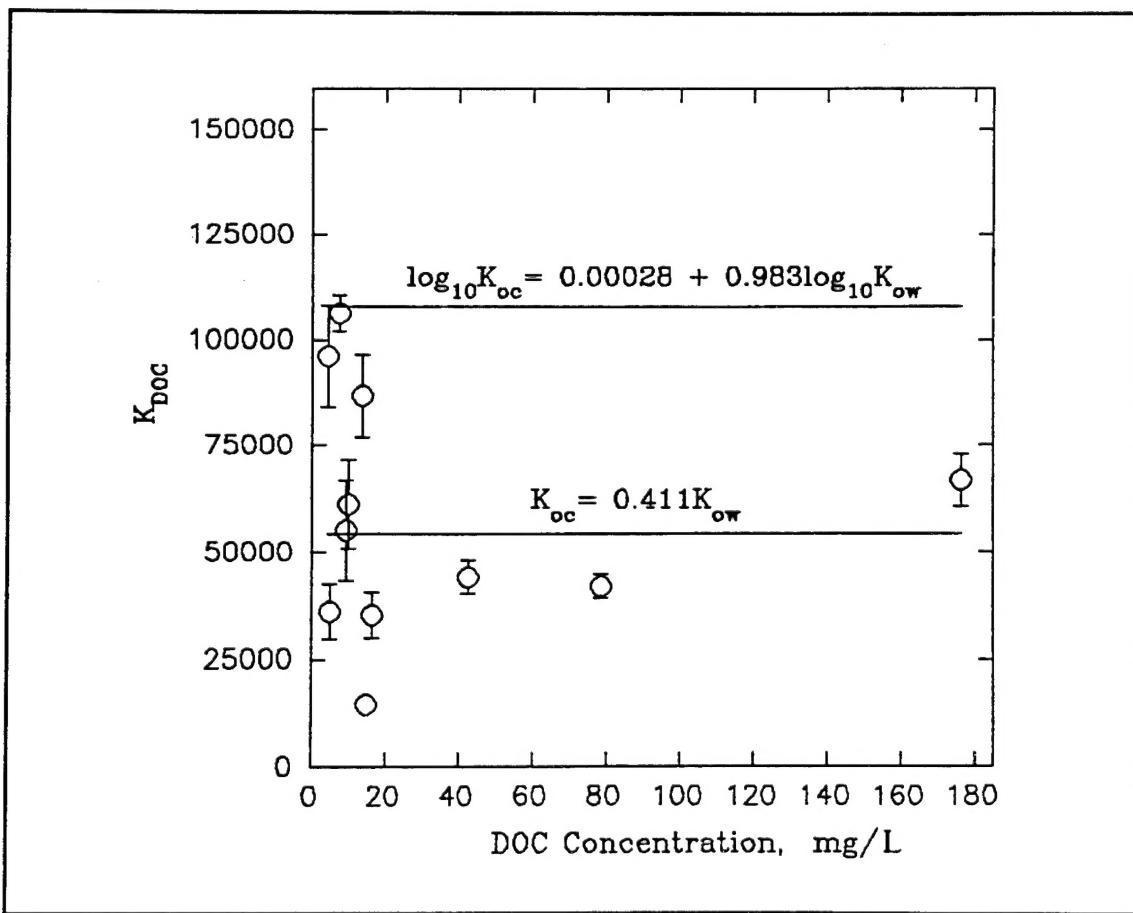


Figure 3. Measured K_{DOC} as a function of pore water DOC concentration. The upper horizontal line represents the DiToro model; the lower horizontal line represents the Karickhoff model. Vertical bars on data points are \pm standard errors of the slope

The concentration of total fluoranthene in solution, C_T , can be expressed as

$$C_T = C_{DOC} + C_d \quad (3)$$

Substituting for C_{DOC} in Equation 1 yields

$$C_T - C_d = m_{DOC} K_{DOC} C_d \quad (4)$$

Solving for C_d gives

$$C_d = C_T / (1 + m_{DOC} K_{DOC}) \quad (5)$$

Use of this equation to predict truly dissolved concentrations of HOCs commonly assumes that $K_{DOC} = K_{oc}$ (DiToro and others 1991). Measured truly dissolved fluoranthene concentrations were compared to concentrations predicted by Equation 5 (Figure 4) using the methods of Karickhoff (1981) and DiToro and others (1991) for deriving K_{oc} . The value of K_{oc} derived from the equation of DiToro and others (1991) substantially underestimated truly dissolved fluoranthene concentrations. The value of K_{oc} derived from the equation of Karickhoff (1981) more closely approximated measured truly dissolved fluoranthene concentrations, but generally over- or underestimated.

Discussion

Measured values of K_{DOC} in sediment pore waters were not constant and were consistently lower than the value estimated by the method of DiToro and others (1991) and the assumption that $K_{DOC} = K_{oc}$. Using the same assumption, the method of Karickhoff (1981) over- and underestimated measured values of K_{DOC} . Differences between measured and estimated K_{DOC} values can be caused by variations in the composition of natural organic matter (Grathwohl 1990, Davis 1993), organic matter aromaticity (Gauthier, Seitz, and Grant 1987), or polarity of pore water organic material (Chiou and others 1986, 1987).

The lack of correspondence of measured values of K_{DOC} with either of the K_{oc} predictive protocols indicates that variations in DOC affect partitioning behavior. Divergence of measured values of K_{DOC} from predicted values indicates that the pore water DOC differs from that of the sediment organic matter for which the relationships relating K_{ow} to K_{oc} were developed. The wide spread of K_{DOC} values measured indicates that the composition of pore water organic matter varied between the sediments investigated. This finding is consistent with several recent reports of wide variation in K_{DOC} values measured in sediment pore water DOC with polycyclic aromatic hydrocarbons (PAHs) (Chin and Gschwend 1992) and soil water soluble DOC with PAHs (Herbert, Bertsch, and Novak 1993).

Evaluation of potential environmental impacts of sediments often involves prediction of truly dissolved concentrations of HOCs in pore water (DiToro

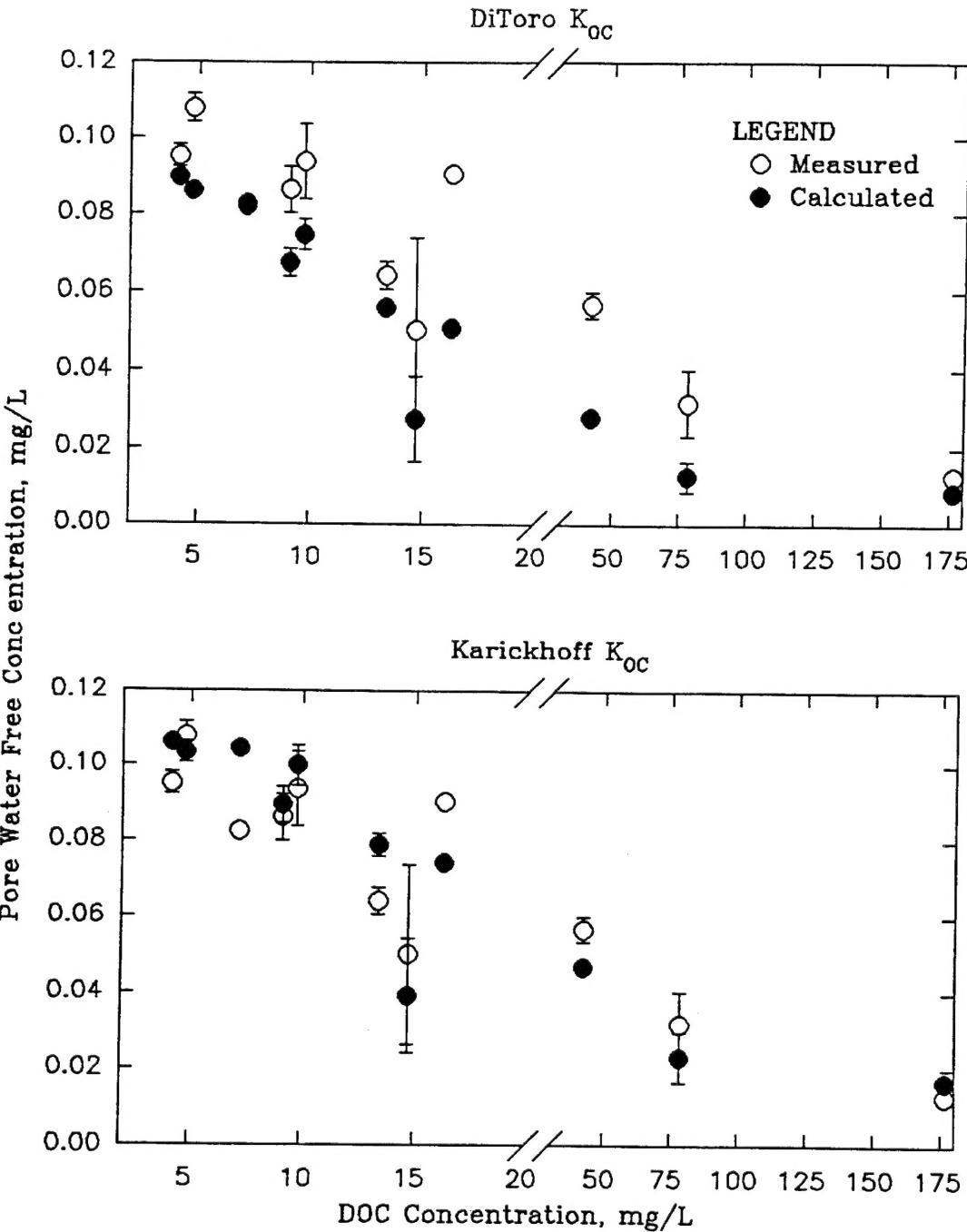


Figure 4. Calculated and measured concentrations of truly dissolved fluoranthene in pore water of varying DOC

and others 1991). Truly dissolved contaminants are usually considered to be the toxic and biologically available fraction of sediment HOC (Landrum and others 1984, Bitton and others 1986).

The divergence of K_{DOC} from values predicted by K_{ow} has implications for prediction of truly dissolved HOCs in pore water. Use of the relationship developed by DiToro and others (1991) relating K_{ow} to K_{oc} consistently underestimates truly dissolved fluoranthene in pore waters. The relationship of Karickhoff (1981) both over- and underestimated fluoranthene pore water concentrations. Use of K_{oc} values to predict truly dissolved concentrations of HOCs in pore water can result in misjudgment of potential environmental impacts.

This study investigated the interactions of only fluoranthene with pore water organic carbon. However, pore water concentrations of other nonpolar organic compounds are likely to exhibit similar behavior (Schrap and Opperhuizen 1989). Models that rely upon the assumption that $K_{oc} = K_{DOC}$ in sediment pore waters should be used with caution until the value of K_{DOC} for sediment pore water can be verified experimentally. The method of Karickhoff (1981) for estimating K_{oc} from K_{ow} in combination with Equation 4 most closely approximated measured K_{DOC} . As illustrated in Figure 2, the spread in sorbed concentrations for a given value of truly dissolved fluoranthene is too extreme to generate an empirical K_{DOC} for pore water. These results are similar to those of Chin and Gschwend (1992), who concluded that an assessment of K_{DOC} must be made on a case-by-case basis when prediction of HOCs in a sediment system is required.

Attempts to extend models developed for the sorption of HOCs by soil and sediment organic matter to dissolved humic substances have been unsuccessful because they consider only the quantity of organic carbon present (Davis 1993). Further study must be directed into the causes of the divergence of measured and estimated values of K_{DOC} .

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